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The role of deposition temperature and catalyst thickness in graphene domains on Cu

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Abstract Few layered graphene is synthesized on Cu foil by thermal chemical vapor deposition. We have investigated the effect of temperature and catalyst's thickness on graphene domain length and number. The synthesized graphene was characterized using Raman spectroscopy and scanning electron microscopy. Raman spectroscopy results show that D-peak intensity increases with an increasing temperature which revealing that some defects have been generated during synthesis on Cu surface synthesis at higher temperature. It also has been observed that increasing in temperatures result in more intense 2D peaks. Although for further rise in temperature, although the number of graphene domain increases and the graphene domain length reduces. Our results provide important guidance toward the synthesis of high quality graphene films.

Keywords Graphene · TCVD · Raman · SEM

Introduction

Despite the advances in graphene research, obtaining a controlled method on film size which can produce larger crystalline graphene domains is still unavailable. This clarifies that researches on graphene growth still needs to be improved. Investigation of structural evolution and growth mechanism can provide guidance to produce desired graphene. The involved parameters in graphene growth have been explored in many studies. High quality single layer and multilayer graphene were synthesized by tuning the growth conditions such as using different gaseous, liquid or solid carbon sources [1], different dilution gases [1, 2] with different flow rates [3], different temperature, process pressure [2], cooling rates [4] as well as catalysts [3], catalyst's thickness, crystallographic orientation [4] and purity states [4, 5]. Thermal chemical vapor deposition (TCVD) of graphene on copper using a gaseous mixture as hydrocarbon source appears to be the most appropriate choice to obtain large area monolayer graphene which can be easily transferred to different substrates in an economical way [6–15]. However, there are some inevitable parameters which are widely degrading the as grown graphene films such as hydrogen concentration, process pressure, hydrocarbon source, catalyst thickness and purity state [14–16].

The aim of this study is to investigate the growth of graphene by TCVD and to understand how the temperature and catalyst's thickness affect the structure and the quality of resulted graphene domains. Graphene domains were produced at different temperatures from 800 to 1000 °C under a ($C_2H_2 + H_2 + Ar = 30/20/900$) flowing gas mixture. Our experiments resulted in growth of few layers graphene domains.

Experimental methods

The graphene films were synthesized by TCVD on both ~50 μm copper foil with (001) crystallographic orientation and ~5 mm copper plate (001) both with ~99.5 %

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purity using methane as the source of carbon. The experimental instrument consists of a quartz tube, a CVD chamber, heating system and channel gas flowing systems. The substrates were cut 1 × 1 cm^2. They have been etched following a common protocol of acetone, alcohol and deionized water. Then they were loaded in TCVD tube. The experiments have been realized under ambient pressure. In order to smooth the substrate surface and to reduce native copper oxide and other impurities on the surface, the samples have been annealed for 20 min under Argon prior to growth process in order to smooth the substrate surface and to reduce native copper oxide and other impurities on the surface. Argon flow was set to be 900 sccm and was kept unchanged during the whole experiment. The annealing temperatures each time were set to be the same as work temperature. Then the growth process started by introducing methane (∼27.5 sccm) together with hydrogen (∼20 sccm) for 10 min. The TCVD treatment were performed at different temperatures 700, 800, 900, 950 and 1000 °C. Once the TCVD growth had finished, the quartz tube was cooled down to room temperature. The graphene quality was characterized quantitatively using Raman spectroscopy and scanning electron microscopy (SEM). The Raman measurements were carried out with SENTERRA (2009) system using a confocal depth profiling with true focus and resolution of 2 μm. The excitation source of Raman spectroscopy was a 785 nm laser with a laser power of 10 mW. The SEM studies of graphene on Cu substrates were performed using HITACHI S 4160 system.

Result and discussion

Experiments have been realized at 700, 800, 900, 950 and 1000 °C. For growth temperature below 800 °C, no graphene has been observed. In order To investigate the effect of Cu substrate thickness, different Cu substrates (Cu foils and 2 Cu plates) have been explored at each temperature. The growth time of 10 min was identical for all samples. From the SEM image (Fig. 1a, b), we one can see the appearance of graphene domains after 10 min of growth.

Darker patches in Fig. 1a, b corresponds to graphene domains and the bright regions are Cu substrate. As it can also be seen, also some additional brighter dots are present which are mostly distributed on Cu substrate (Fig. 1b). This has been partially observed on Cu plate as well (Fig. 1c).These brighter dots are preferred to stay at the step edges in region where no graphene-coating occurred. These scattered dots are would be more intensively present with further increasing of the temperature (Figs. 3c, 5c, 6b). The presence of these dots reveals that the grown film is probably graphene/Cu_xO film [4]. It has been reported that the quantity of Cu_xO nanodots and the quality of grown graphene is highly dependent on growth pressure. At relatively low pressure (∼80 Pa), a large quantity of Cu_xO nanodots appears on graphene domain boundaries. At relatively higher pressure which is the case in this work, the graphene grows much faster and saturates the copper surface quickly which leading to a low density of Cu_xO as it can be seen in Figs. 1, 3, 5 and 6.

Moreover, the methane-to-hydrogen ratio (r) in this work was kept to be at 1.5. For such a low methane concentration, nanodots are reported to be more prevalent which can suppress the growth of continuous graphene coverage [4]. For further rise in temperature up to 900, 950 and 1000 °C, more areas with graphene domains can be observed (Figs. 3, 4, 5). Although SEM images show the well-defined graphene domains on Cu plates at 900 °C (Fig. 3d), however this is not the case for sample deposited at higher temperatures. For deposition temperature more than 900 °C, the samples are fully covered by small graphene domains.

Graphene domain length L_a can be estimates using the relation below [16, 17]:

$$I_D/I_G = C(\lambda)/L_a \quad (1)$$

where $C\ (\lambda) = 2.4 \times 10^{-4}$ and λ is the wavelength of Raman laser, I_D and I_G are the intensities of the D-band and G-band respectively.

The calculated graphene domain length is plotted in Fig. 2. The length of graphene domain for 800 °C deposited graphene on Cu foil is about 35 nm. Further increasing in temperature up to 900 °C gives larger graphene domain about 65 nm. However, 950 and 1000 °C deposited samples have smaller graphene domains. Figure 2 also shows that at each given temperature, graphene domains on Cu plate are larger than graphene domains on Cu foil. At 800 °C, the graphene domain length on Cu plate is around 55 nm while it is around 35 nm for Cu foil. These values increase up to 70 nm for Cu plate and 65 nm for Cu foil deposited at 900 °C. However, the calculated length of graphene domains for samples deposited at 950 °C decrease to ∼40 nm for Cu foil and to ∼35 nm for Cu plate.

Although at relatively high temperatures, the graphene domains length is to be reduced, however their number increases. SEM images show large number of graphene domains for deposition temperatures of 950 and 1000 °C. They also reveal that these graphene domains have irregular shape which also has been reported elsewhere (Figs. 5 and 6) [12, 18]. At any given temperature, graphene is known to preferentially nucleate on surface irregularities and impurities, such as foil processing grooves which lead to small sizes of graphene domains [14–16]. SEM images of samples deposited at 950 and 1000 °C (Figs. 5 and 6)

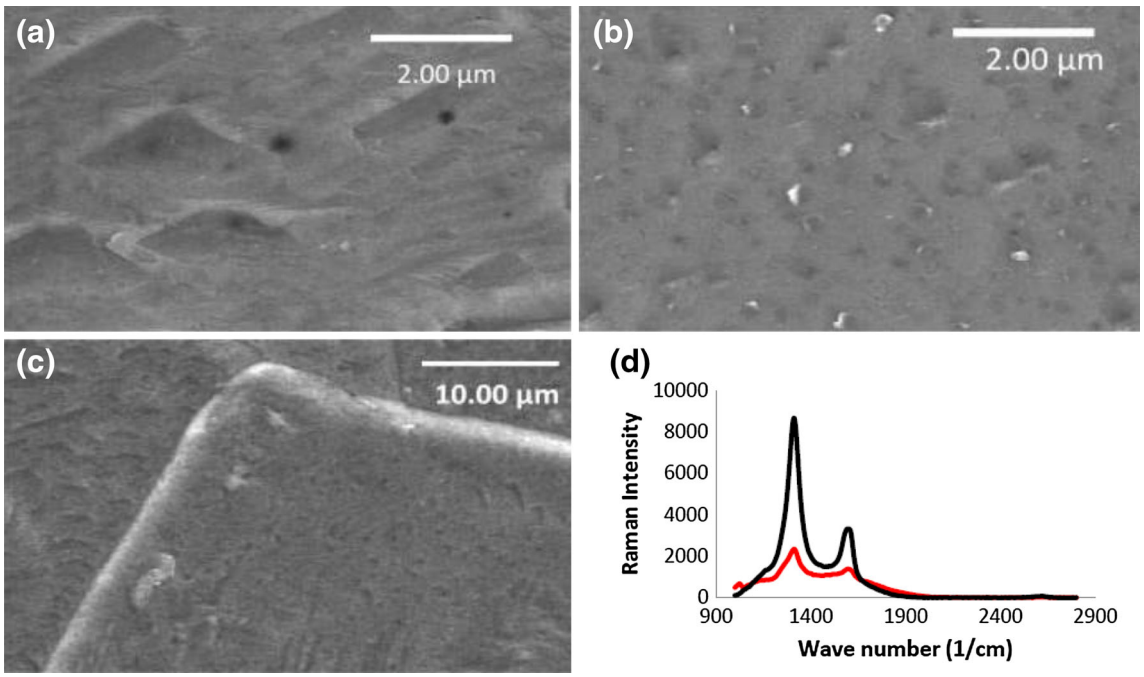

Fig. 1 Scanning electron microscope images of graphene domains on **a** and **b** Cu foil at different scales, **c** Cu plate at 800 °C. **d** Corresponding Raman spectra of the same samples, *black* and *red curves* describe graphene domains on Cu foil and Cu plate respectively

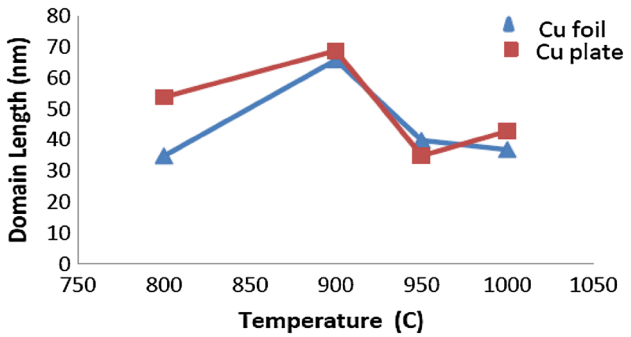

Fig. 2 Calculated graphene domain length

show numbers of carbon islands nucleated around impurity particles on the Cu surface.

A typical Raman spectroscopy of sample deposited at 800 °C is presented in Fig. 1d which identifies few layer graphene. It shows a D-peak at $\sim$1312 cm^{-1} and a G-peak at $\sim$1595 cm^{-1}(for both Cu plate and Cu foil grown graphene). Also the D-band intensity in both cases is much stronger than that of G-band with I_D/I_G of about 2.6 for Cu foil and 1.7 for Cu plates grown graphene. The full width at half-maximum (FWHM) of the G-band for Cu foil grown graphene is about $\sim$100 cm^{-1}. However, the defect-induced D-band intensity is strong with FWHM of about $\sim$80 cm^{-1}. It has been reported that as the number of graphene layers increase, the D-peak should be are normally encountered [19]. In general, for all samples Raman spectra show that the D peak intensity increases with an increasing in temperature. It can be concluded that some defects have been generated during synthesis on Cu surface at higher temperature (Figs. 1d, 3b, 5d, 6d).

The Raman spectra of the samples deposited at 900, 950 and 1000 °C (Figs. 3b, 5d, 6d) illustrate similar growth for both Cu catalysts except for 2D-band. Figure 4 shows Raman spectra near 2D peaks region for samples deposited at 900, 950 and 1000 °C. As it can be seen, increasing in temperature results in more significant 2D-peaks intensity. The intensity of 2D-peak varies from $\sim$80 (au) for sample deposited at 900 °C to $\sim$800 (au) for sample deposited at 1000 °C. Although increasing the temperature results in smaller graphene domains, the intensity of 2D-peak as well as the density of graphene domains increases. One can conclude that higher temperature may produce higher density of smaller graphene domains which may laterally join together and fully cover the catalyst surface.

For graphene domains on Cu foils for example, 2D-peaks are presented at 2605.5 cm^{-1} with FWHM of $\sim$90 cm^{-1}, 2615.5cm^{-1} with FWHM of $\sim$150 cm^{-1}, 2609.5 cm^{-1} with FWHM of $\sim$200 cm^{-1} for 900, 950 and 1000 °C respectively (Fig. 4). According to Nasir K. Momen et al., the 2D band of single layer graphene occurs at about $\sim$2660 cm^{-1} and a 2D peak around this wave number is typically associated with few layer graphene [19] which has also been reported elsewhere [15, 17].

Since the shape of the 2D band reflects the electronic band structure of the graphene lattice according to Refs. [20, 21], we can infer that the electronic band structure of

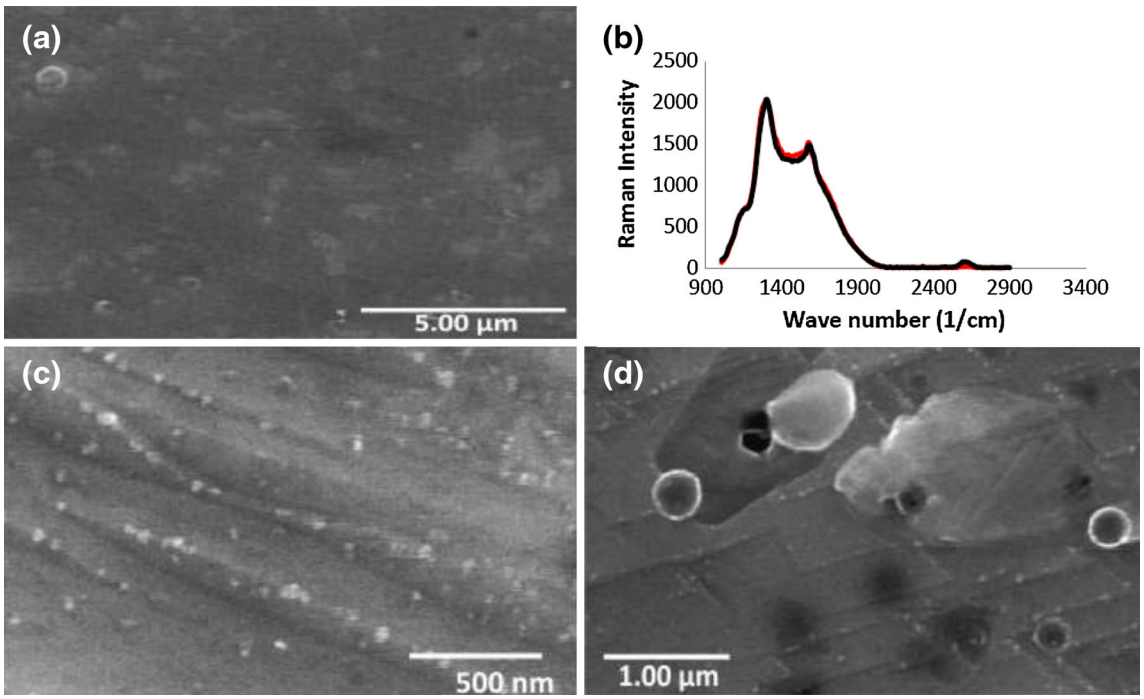

Fig. 3 Scanning electron microscope images of graphene domains on **a** Cu foil, **c** and **d** Cu plate at 900 °C. **b** Corresponding Raman spectra of the same samples, *black* and *red curves* describe graphene domains on Cu foil and Cu plate respectively

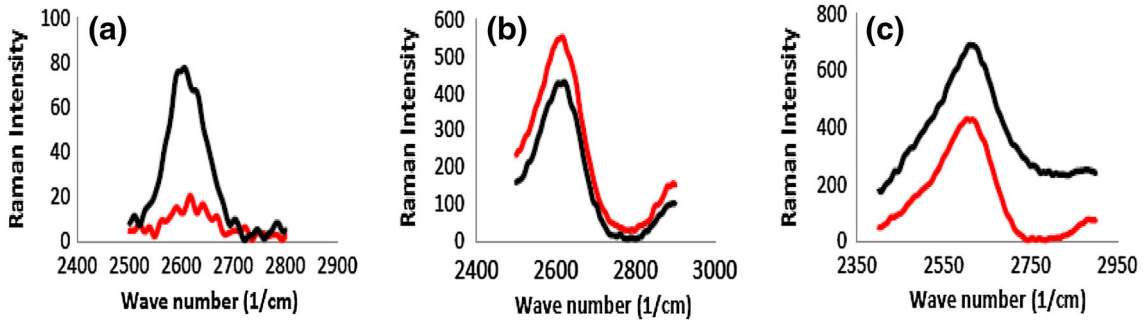

Fig. 4 Raman spectra of **a** samples deposited at 900 °C and **b** samples deposited at 950 °C and **c** samples deposited at 1000 °C. *Black* and *red curves* correspond to graphene grown on Cu foil and Cu plate respectively

few layers of graphene is very similar to graphite. There is also an overall shift of the 2D band with increasing number of layers. Therefore, by combining the intensity images of the G and the 2D bands, one can reliably estimate the number of graphene layers, whiles It is known that the distance between graphene layers is about 0.335 nm in graphite lattice.

Conclusion

We have investigated the effect of temperature and catalyst's thickness on graphene domain length and number. For deposition temperature below 800 °C, no graphene formation has been observed. SEM images show the appearance of graphene domains after 10 min of growth for temperatures above 800 °C. The presence of some bright nanodots in SEM images reveal that the grown film is probably graphene/Cu_xO film. From 800 to 900 °C, graphene domain length increases. For further rise in temperature, the number of graphene domain increases the graphene domain length reduces. Moreover, at each given temperature, graphene domains on Cu plates are larger than graphene domains on Cu foil. Raman Spectroscopy results show that D-peak intensity increases with an increasing the temperature which reveals that some defects have been generated during synthesis on Cu surface at higher temperatures. It also has been observed that increasing in

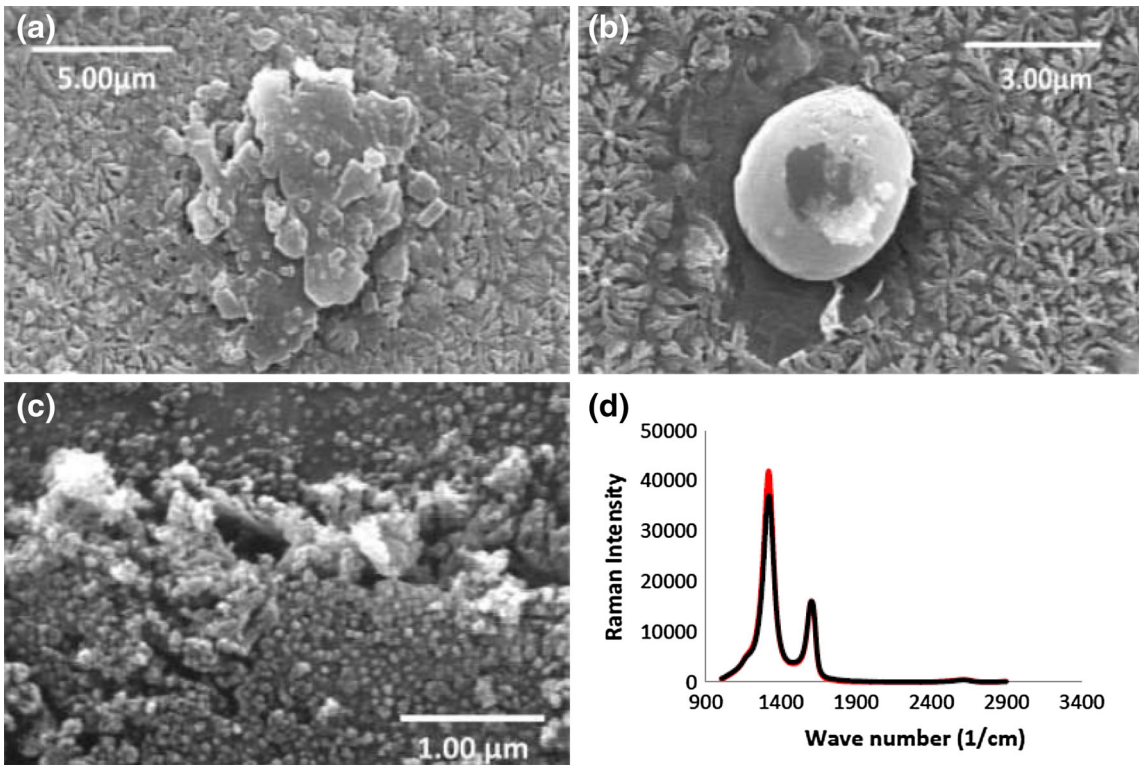

Fig. 5 Scanning electron microscope images of graphene domains on **a** and **b** Cu foil, **c** Cu plate at 950 °C. **d** Corresponding Raman spectra of the same samples, *black* and *red curves* describe graphene domains on Cu foil and Cu plate respectively

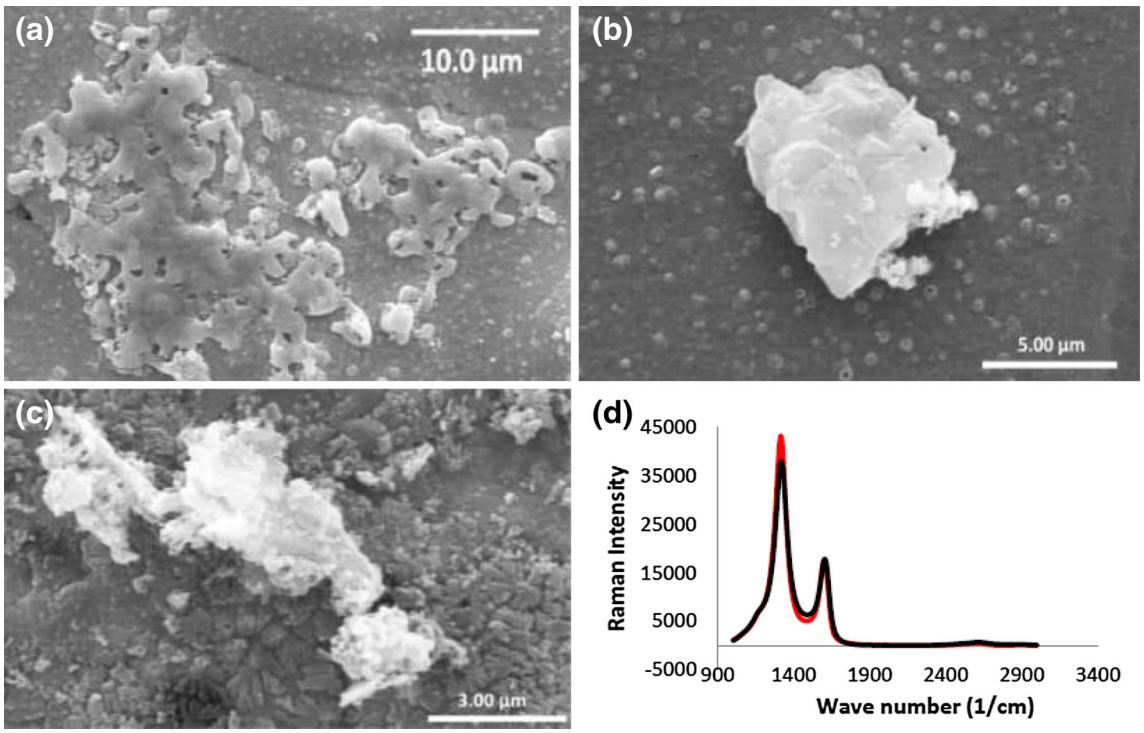

Fig. 6 Scanning electron microscope images of graphene domains on **a** and **b** Cu foil, **c** Cu plate at 1000 °C. **d** Corresponding Raman spectra of the same samples, *black* and *red curves* describe graphene domains on Cu foil and Cu plate respectively

temperatures results in more intense 2D peaks. This latter indicating that further increasing in temperature may result in fully coverage of catalyst surface by graphene.

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